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THE VISCOSITIES AND DENSITIES OF CHLOROSULPHONIC ACID – SULPHUR TRIOXIDE MIXTURES[1]

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Abstract

The viscosities and densities of crude chlorosulphonic acid – sulphur trioxide mixtures have been determined for compositions between 10 and 70%. The viscosity measurements were carried out at temperatures between 20° and −40° C. for those liquids that did not show crystallization over this range. At temperatures at which the complete range of compositions could be investigated, both the density– and viscosity–composition curves exhibit a maximum.

Introduction

No previous reports of measurements of the viscosity of mixtures of sulphur trioxide and chlorosulphonic acid appear in the published literature. The work reported here was undertaken to provide such data for this system. Since it was desired to obtain values applicable to commercial materials, all measurements were made on the commercial products without preliminary purification.

Apparatus, Experimental Procedure and Materials

All measurements were carried out in a constant temperature bath that consisted of a Dewar flask filled with gasoline and fitted with a toluene filled thermometer (calibrated against a platinum resistance thermometer), a stirrer, a thermoregulator, and a cooling coil. The thermoregulator controlled a small centrifugal pump that circulated gasoline through the cooling coil from an auxiliary cooling bath. The latter was cooled with dry ice to a temperature a few degrees below that desired in the constant temperature bath. With such an arrangement, it was observed that the temperature remained constant to $\pm$ 0.1° C. in the temperature range from 20° to −40° C.

The viscosity measurements were made with two Ostwald type viscosimeters fitted with phosphorus pentoxide tubes to prevent absorption of atmospheric moisture by the very hygroscopic liquids that were under investigation. The flow of the liquid in the viscosimeter was observed from above by means of two small mirrors attached to the viscosimeter tube at an angle of 45°.

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The constants for these viscosimeters were obtained using two standard oils of known viscosity supplied by the United States Bureau of Standards.

The densities of the liquids were measured using a modification of the standard Sprengel specific gravity tube. It was furnished with an additional bulb blown in one of the side arms above the filling mark to allow for the expansion of the liquid as it warmed up from the low temperature at which the measurement was made to the temperature of the balance. To prevent absorption of water vapor from the atmosphere, the arms were equipped with ground-glass caps.

As the primary object of this work was to obtain viscosity data applicable to commercial products, all measurements were made on the crude materials, with no preliminary purification. The following materials were used in preparing the mixtures.

(*a*) A mixture of chlorosulphonic acid and sulphur trioxide received from Suffield Experimental Station. Analysis by a method described later gave chlorosulphonic acid 45.51%, sulphur trioxide 54.25%, undetermined 0.24%.

(*b*) Practical grade chlorosulphonic acid supplied by the Eastman Kodak Company.

(*c*) Sulphur trioxide supplied by Suffield Experimental Station. When received it was in the form of a dark solid, which was melted before use.

Two series of mixtures were prepared, with compositions ranging from approximately 10% to 70% sulphur trioxide. Series *A* mixtures were prepared by the addition of either sulphur trioxide or chlorosulphonic acid to the commercial mixture, while Series *B* liquids were prepared by the direct addition of sulphur trioxide to chlorosulphonic acid.

The mixtures so prepared were analyzed by the following method. A small glass bulb was blown on a piece of glass tubing having a capillary tip. After weighing, the bulb was warmed slightly and the capillary tip was placed in the liquid to be analyzed. After some liquid had been drawn into the bulb, the capillary was sealed and the bulb and contents weighed, the increase in weight giving the weight of the sample. The filled sampling bulb was then placed in a 500 ml. glass stoppered Erlenmeyer flask containing a small amount of distilled water, and the bulb was broken by shaking. When the vapors formed had been absorbed by the water, the solution was titrated with standard sodium hydroxide solution, using phenolphthalein as the indicator. The end point of this titration having been reached, the sample was next titrated with standard silver nitrate solution using Fajan's method.

The weight of chlorosulphonic acid was calculated from the chloride analysis, and the weight of sulphur trioxide from the acidity not accounted for by the chlorosulphonic acid. The results of these analyses are given in Tables I and II.

Results and Discussion

The densities of the mixtures in Series *A* were measured at 20° and 0° C. while the Series *B* mixtures were measured at 20°, 0°, −10°, and −20° C. The results are given in Tables I and II, respectively. For the calculation of the viscosities, the values of the densities at other temperatures were obtained by assuming a linear relation between density and temperature over the range investigated.

TABLE I

COMPOSITION AND DENSITIES OF CHLOROSULPHONIC ACID – SULPHUR TRIOXIDE MIXTURES

Series *A*

Sample No.	Composition			Density, gm./cc.	
	% HSO_3Cl	% SO_3	% Undetermined	0° C.	20° C.
*A*1	86.65	12.80	0.55	1.824	1.794
*A*2	76.65	23.06	0.48	1.865	1.834
*A*3	65.23	34.49	0.28	1.909	1.874
*A*4	55.04	44.43	0.53	1.943	1.906
*A*5	45.51	54.25	0.24	1.967	1.925
*A*6	36.88	62.77	0.35	1.981	1.932
*A*7	28.10	71.06	0.84	1.992	1.941

TABLE II

COMPOSITION AND DENSITIES OF CHLOROSULPHONIC ACID – SULPHUR TRIOXIDE MIXTURES

Series *B*

Sample No.	Composition			Density, gm./cc.			
	% HSO_3Cl	% SO_3	% Undetermined	20° C.	0° C.	−10° C.	−20° C.
*B*1	89.15	10.92	—	1.783	1.813	1.827	1.843
*B*2	77.86	22.12	0.02	1.824	1.855	1.870	1.885
*B*3	67.83	31.87	0.30	1.860	1.891	1.906	1.924
*B*4	57.97	41.37	0.66	1.892	1.926	1.942	1.959
*B*5	48.50	51.09	0.41	1.917	1.955	1.973	1.990
*B*6	38.89	59.58	0.53	1.936	1.978	1.998	2.015
*B*7	31.36	68.45	0.19	1.943	1.989	2.013	—

The results of the viscosity measurements on the mixtures of Series *A* and Series *B* are given in Tables III and IV, respectively. The determinations were carried out at temperatures down to −40° C., unless crystallization occurred before this temperature was reached.

TABLE III

VISCOSITIES OF CHLOROSULPHONIC ACID – SULPHUR TRIOXIDE MIXTURES

Series *A*

Sample No.	Viscosity, millipoises			
	20° C.	0° C.	−20° C.	−40° C.
*A*1	46.8	77.1	147.9	385.7
*A*2	58.7	108.2	241.7	837.1
*A*3	83.6	177.4	479.8	2411.0
*A*4	108.8	274.4	952.6	7335.0
*A*5	120.8	344.4	1537.0	17360.0
*A*6	117.8	372.8	1931.0	—
*A*7	108.4	378.4	—	—

TABLE IV

VISCOSITIES OF CHLOROSULPHONIC ACID – SULPHUR TRIOXIDE MIXTURES

Series *B*

Sample No.	Viscosity, millipoises						
	20° C.	10° C.	0° C.	−10° C.	−20° C.	−30° C.	−40° C.
*B*1	39.3	48.8	62.7	85.4	117.3	176.2	294.1
*B*2	56.0	71.7	98.3	140.7	209.2	353.7	695.2
*B*3	81.9	103.8	149.9	233.5	384.2	735.3	1683.0
*B*4	104.8	155.0	239.8	410.7	775.1	1721.0	4881.0
*B*5	129.6	204.9	352.3	669.5	1401.0	3751.0	12710.0
*B*6	136.8	232.8	434.6	933.0	2302.0	7205.0	—
*B*7	121.8	216.8	425.4	—	—	—	—

Since the measurements on the Series *B* liquids were carried out over a wider temperature range than on those of Series *A*, only the former are presented in graphical form.

Fig. 1 shows the density of the Series *B* liquids as a function of the percentage of sulphur trioxide. Included in this plot are the densities of the pure components chlorosulphonic acid and sulphur trioxide at 20° C. as given in the International Critical Tables. In the curve for 20° C., the only one that covers the complete range of composition from 0% to 100%, it is seen that a maximum in the density must occur at a composition above 70%.

In Fig. 2, the logarithm of the viscosity is plotted against the percentage of sulphur trioxide for the mixtures in Series *B*. The results at 0°, 10° and 20° C., the only temperatures at which mixtures containing more than 60% SO_3 could be investigated because of crystallization, indicate that a maximum in the viscosity–composition curve occurs at about 60% SO_3. Although this composition corresponds approximately to the formula $HSO_3Cl \cdot 2SO_3$, the existence of a maximum in the viscosity–composition curve at this point is not necessarily indicative of compound formation. Many mixtures are known (1) that exhibit such a maximum, in the absence of the formation of definite compounds.

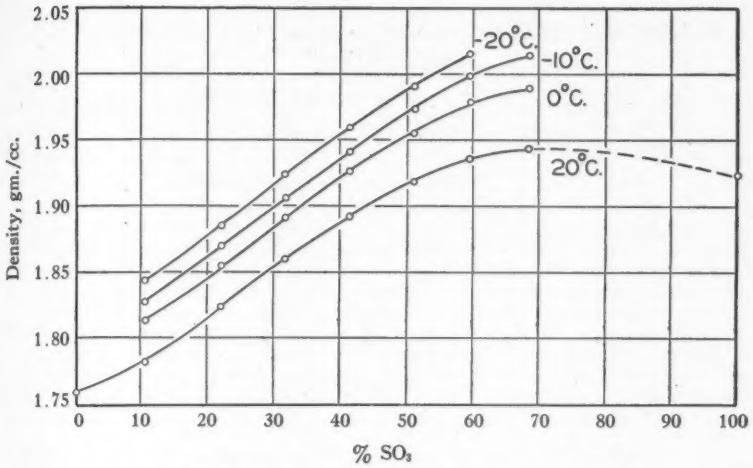

FIG. 1. *Densities of chlorosulphonic acid – sulphur trioxide mixtures.*

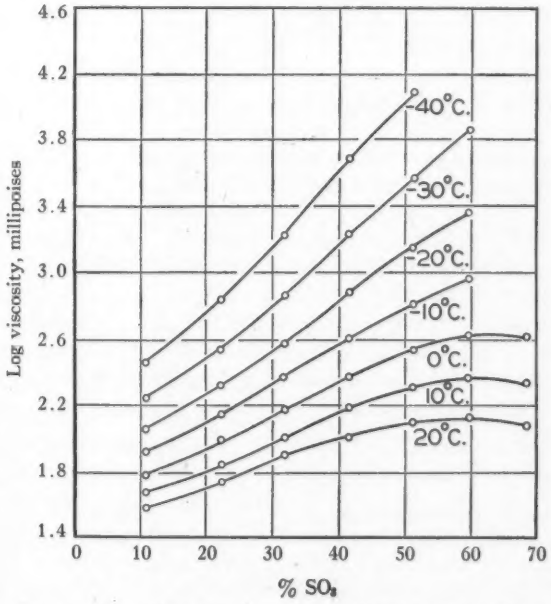

FIG. 2. *The logarithm of the viscosity of chlorosulphonic acid – sulphur trioxide mixtures.*

Reference

1. HATSCHEK, E. The viscosity of liquids. G. Bell and Sons, Ltd., London. 1928.

A STUDY OF THE PRO-KNOCK ACTIVITY OF VARIOUS SUBSTANCES[1]

By J. D. B. Ogilvie,[2] S. G. Davis[3], A. L. Thompson,[4] W. T. Grummitt,[5] and C. A. Winkler[6]

Abstract

Compounds that cause an increase in the knocking tendency of gasolines are of two main types: (1) those such as dichloromethylarsine, cacodyl chloride, and arsenic tribromide, which counteract the effect of antiknock compounds present, and (2) those which, in addition, have some effect on the base stock, such as chloropicrin, bromopicrin, and bromine. Halogens, nitrites, nitro compounds and elements of Group V add to the pro-knock properties of a molecule. A long chain and an asymmetric molecule are effective structures. Pro-knock neutralized the effect of the antiknock but the concentration bore no direct relation to the antiknock concentration. Compounds of the first type showed greatest effect in fuels of high lead susceptibility brought up to a high octane rating with lead tetraethyl from a low octane base stock. They were similarly effective in counteracting iron carbonyl, but had no effect on aniline. Compounds of the second type effectively counteracted aniline, and when added to Diesel fuels showed a marked increase in the cetene number.

Introduction

The combustion of hydrocarbons is a complex process, as indicated by the variety of products that can be isolated. Most investigators are agreed that the mechanism is of the chain reaction type (1, p. 2927; 2; 3). The reaction chain may divide or branch, giving rise to new centers of activity. The process may then be expected to be highly susceptible to the influence of active catalysts and of changes in the temperature, pressure, and other conditions prevailing in the combustion chamber. An accumulation of extremely active chain carriers or other active intermediate products may occur during the early stages of the burning and give rise to a knocking type of combustion. This is a violent detonation of the last portion of the charge and occurs in internal combustion engines mainly when the engine is operating at high compression ratios and at low speed due to heavy load (4; 5, p. 3024; 7).

The variation in the knocking propensity of gasolines of various chemical compositions is well known (5, p. 3024; 6; 7), in particular the effects of such factors as the molecular chain length and branching, the degree of unsaturation,

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and the cyclic or aromatic nature of the fuel. The octane rating for comparison of the knocking characteristics of gasolines and its measurement requires no discussion here.

The action of antiknock compounds such as lead tetraethyl (8, p. 2911; 9, p. 692; 10), iron carbonyl (11, 12) and aniline (14) is also a matter of common knowledge. When present in small quantities these compounds result in a considerable improvement in the combustion characteristics of gasolines, from the point of view of power developed by, and smoothness of operation of, the engine. The action of pro-knock compounds is less well known, although substances such as ethers (12), peroxides (15), and organic nitrites, nitrates, and nitro compounds (13, 16, 17) are reported to promote knocking when present in a gasoline in low concentrations.

The investigations reported herein follow two lines of approach:

(*a*) A study of the relative pro-knock activity of various compounds by determining the concentrations necessary to cause a 10 octane decrease in the rating of an 80 octane aviation fuel, particularly when the pro-knock was introduced into the air intake of an internal combustion engine.

(*b*) A study of the effects of various pro-knock compounds on leaded and unleaded gasolines of different base stocks to observe their effects on these various types of fuels, and to obtain a clearer picture of the modes of action of the pro-knock substances.

The Pro-Knock Activity of Various Compounds

Preliminary Experiments

For the preliminary experiments a 1933 model Chevrolet engine was used. This was operated with a suitable braking arrangement at low speed and full throttle. Under these conditions the engine was extremely sensitive to pro-knock compounds. The addition agents were introduced into the air intake of the engine by placing a piece of gauze, wetted with the material, over the intake pipe. Some 197 compounds were tested. Those that caused knocking were investigated further. Measured quantities were introduced by displacement from a burette and subsequent atomization and evaporation in the air intake of the engine. The audibility of knock was used to compare the activity of various materials.

Procedure

Later work was done using an Ethyl Knock Testing Engine, Type 30B. This machine, although obsolete for routine laboratory testing, proved to be quite satisfactory. Results obtained in checking the octane ratings of gasoline agreed closely with those determined by the supplier. Operating conditions were those recommended in the operating manual for fuels in the octane range under study.

For every compound examined at least five octane determinations were necessary to establish a curve of octane decrease with concentration. Since the standard method of determining the octane ratings takes about two hours, it was desirable to decrease this time to speed up the investigation. Although the knockmeter reading for a gasoline of given octane rating may vary appreciably over the time necessary to complete the investigation of one addition agent, it was found that throughout this period the knockmeter range for two fuels of octane rating, say 10 units apart, remained essentially constant. Consequently the procedure adopted was as follows.

(*a*) Calibration of knockmeter over the desired range using standard reference fuels. A plot of knockmeter change versus octane change was made.

(*b*) Determination of the knockmeter reading for the basic fuel. (Each new shipment of gasoline was standardized by the usual Co-operative Fuel Research Method.)

(*c*) Alternate determination of the knockmeter readings for the several tests on an adulterant and on the base fuel. The octane change was readily determined from the calibration.

(*d*) The calibration was checked daily or when it appeared to have changed.

Since solid, liquid, and gaseous compounds were investigated as adulterants, various techniques were required to admit their vapors into the air consumed by the engine. The apparatus used is shown diagrammatically in Fig. 1.

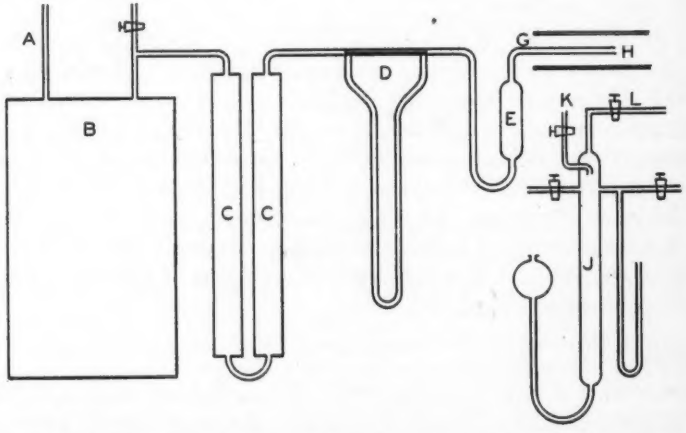


FIG. 1. *Apparatus for introducing adulterants. A, compressed air supply; B, surge capacity; C, calcium chloride and phosphorus pentoxide drying tubes; D, capillary type flowmeter; E, pycnometer containing liquid adulterant; G, inlet tube to knock testing engine; H, air intake of engine; J, burette containing gaseous adulterant; K, to mercury or sulphuric acid displacing liquid reservoir; L, inlet tube to engine.*

1. *Liquids*—were introduced by bubbling a small regulated stream of dry air through the compound contained in a pycnometer fitted with ground glass caps. When necessary the pycnometer was heated electrically or cooled by a dry ice and acetone bath. The engine was operated for 10 min. at each of five concentrations of adulterant, knockmeter readings being recorded. The concentration was regulated by the air stream and determined by the loss in weight of the pycnometer. The concentration necessary to cause a 10 octane drop was determined from a plot of octane decrease versus concentration.
2. *Solids*— were introduced similarly, using a horizontal pycnometer. Electrical heating was employed when necessary.
3. *Gases*— were added to the air stream by displacement from a burette attached to the inlet tube. Atmospheric pressure was maintained by a suitable leveling bulb and manometer system. In some cases the gas was diluted with air to a known concentration before displacement.

For solution work a stock solution of the adulterant in the basic fuel was made, and diluted portions were tested in progressively increasing concentrations until a 10 octane drop occurred. The concentration could be expressed in terms of the air consumption from the air–fuel consumption ratio curve obtained experimentally.

The gasoline used in this study was an 80.5 octane fuel leaded from a 72.5 octane aviation base stock using about 1.5 cc. of lead tetraethyl per U.S. gallon.

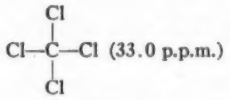
Adulterants were obtained from a variety of sources, a considerable number being prepared by the division of organic chemistry, McGill University, under the direction of Dr. R. V. V. Nicholls.

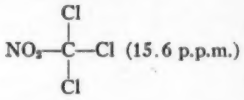
Results

The data obtained on the concentration of adulterant, expressed as parts per million of the air consumed by the engine, to cause a 10 octane decrease are recorded in Table I. The most effective materials of those studied are dichloromethylarsine (3.8 p.p.m.), arsenic tribromide (4.6 p.p.m.), cacodyl chloride (4.2 p.p.m.), lewisite (4.6 p.p.m.), and arsenic trichloride (5.8 p.p.m.). Other arsenic and phosphorus halides and oxyhalides are very effective and also some halogen–nitro substituted hydrocarbons. From the data obtained the following deductions may be made.

(1) The middle Group V elements of the periodic table possess the greatest pro-knock activity. The decreasing order of activity appears to be arsenic, phosphorus, nitrogen, and antimony. Vanadium in Group V(*a*) is between arsenic and phosphorus in pro-knock properties, as is its atomic weight. These elements are most effective as the halide or oxyhalide or in metallo-organic

molecules with halogens also present. Nitrogen in organic nitrites, nitrates, and nitro compounds shows considerable effectiveness. The inclusion of a nitro group in an organic halide greatly enhances the effect of the halogen, e.g.,





(2) The halogens possess powerful pro-knock tendencies by themselves and in combination with other elements. The order of decreasing effectiveness, both in the elemental and combined state, appears to be: bromine, chlorine, iodine, and fluorine. Both organic and inorganic halogen compounds are effective; for example, arsenic trichloride and chloropicrin. This would indicate, as do the data on arsenic, that the element itself rather than the type of linkage is important. Among the chloromethanes and chloroethanes, the activity increases with the number of chlorine atoms in the molecule. The tri-, penta-, and oxychlorides of phosphorus or arsenic have essentially similar pro-knock activity. Iodine mono- and trichlorides are considerably more effective than either iodine or chlorine as elements.

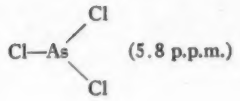
(3) Among the Group VI elements, chromium, as the oxychloride, is as effective as phosphorus. Sulphur is also quite effective, as shown by the compounds sulphur chloride (10.6 p.p.m.), thionyl chloride (15.1 p.p.m.), methyl disulphide (37 p.p.m.) and *n*-butyl mercaptan (108 p.p.m.). The sulphide linkage appears to be more effective than the mercaptan. Ethyl sulphite is more effective than ethyl nitrate. The thionitrites are not as effective as the nitrite, and the thiocyanate is much more effective than the isothiocyanate. Selenium seems even more effective than sulphur when used as the oxychloride (8.3 to 15.1 p.p.m.).

(4) Other elements that appear to show good pro-knock activity are aluminum (aluminum chloride, 14.5 p.p.m.) and silicon (silicon tetrachloride, 33.0 p.p.m.).

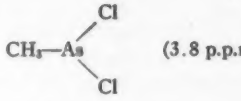
(5) The metal naphthenates, when added in solution, give a good comparison of the relative activities of the metals themselves since the naphthenate radical has very slight antiknock properties. Mercury and vanadium are particularly effective and chromium, nickel, iron, and copper less so. Magnesium, zinc, lead, manganese, and cobalt are not very effective.

(6) Studies of the organic halides, nitrites, and nitro compounds show that increasing the straight chain length in aliphatic compounds increases the pro-knock activity of the molecule (e.g., chlorides—methyl 195, ethyl 156, heptyl 88; nitrites—methyl 300, ethyl 200, heptyl 49). Branching, as illustrated by the butyl and amyl nitrites, decreases the effectiveness of the compound.

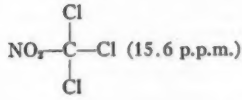
(7) The inclusion of a methyl group in arsenic trichloride, as dichloromethylarsine, results in increased activity. This is true, also, with chloropicrin and 1,1,-dichloronitroethane.



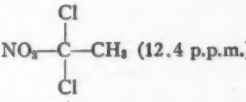
(5.8 p.p.m.)



(3.8 p.p.m.)



(15.6 p.p.m.)



(12.4 p.p.m.)

(8) Aromatic compounds are, in general, poor pro-knock materials. Benzene sulphonyl chloride requires 54 p.p.m. to cause a 10 octane decrease even with the active sulphonyl chloride substituent.

TABLE I

PRO-KNOCK CONCENTRATIONS FOR 10 OCTANE DECREASE

(Expressed in parts per million of air consumed)

Compound	In air, p.p.m.	In fuel, p.p.m.	Compound	In air, p.p.m.	In fuel, p.p.m.
Organic nitrites					
Methyl nitrite	300.0		Nitrite of *sec*-butyl carbinol	92.0	
Ethyl nitrite	200.0		Nitrite of diethyl carbinol	93.0	
n-Butyl nitrite	82.5	67.0	*n*-Propyl nitrite	125.0	
Isobutyl nitrite	107.0		*n*-Heptyl nitrite	49.0	
sec-Butyl nitrite	88.0		*n*-Octyl nitrite	45.0	62.5
tert-Butyl nitrite	96.5		Trichloroethyl nitrite	76.0	
n-Amyl nitrite	62.0		*n*-Butyl thionitrite	130.0	
Isoamyl nitrite	63.0	74.5			
tert-Amyl nitrite	92.0				
Organic halides					
Monochloromethane	195.0		Trichloroethylene	51.0	
Dichloromethane	68.0	68.5	Tetrachloroethylene		41.5
Trichloromethane (chloroform)	44.0	62.5	*tert*-Butyl chloride		45.5
Carbon tetrachloride	33.0	40.0	*n*-Heptyl chloride	88.0	
Difluorodichloromethane (freon)	125.0		Benzyl chloride	141.0	
Dibromomethane	48.3		Oxalyl chloride	45.1	
Monochloroethane	156.0	156.0	Carbonyl chloride (phosgene)	120.0	
1,1-Dichloroethane	78.0		Ethyl hypochloride	135.0	
1,1,2-Trichloroethane	55.0	67.0	Cyanogen bromide	113.0	
1,1,2,2-Tetrachloroethane		40.5	Chloral cyanohydrin	37.0	
Pentachloroethane		27.0	Trichloroacetyl chloride	28.0	
Hexachloroethane	16.4		Ethylene chloronitrite	150.0	
1,2-Dichloroethylene		63.0	Trichloroethyl nitrite	76.0	
			Diethylchloramine	164.0	

TABLE I—*Concluded*

PRO-KNOCK CONCENTRATIONS FOR 10 OCTANE DECREASE—*Concluded*

(Expressed in parts per million of air consumed)—*Concluded*

Compound	In air, p.p.m.	In fuel, p.p.m.	Compound	In air, p.p.m.	In fuel, p.p.m.
Halogens and inorganic halides					
Chlorine	40.0		Selenium oxychloride	8.3	43.5
Bromine	16.2		Phosphorus trifluoride	31.5	
Iodine	56.0		Phosphorus pentafluoride		41.1
Hydrogen fluoride	90.0		Phosphorus trichloride	8.6	
Hydrogen chloride	30.0		Phosphorus pentachloride		6.5
Hydrogen bromide	62.0		Phosphorus oxychloride	8.7	26.5
Iodine monochloride	18.5		Arsenic trifluoride	11.0	
Iodine trichloride	11.8		Arsenic trichloride	6.8	
Iodine monobromide	15.5		Arsenic pentachloride	6.1	
Boron trifluoride	115.0		Arsenic tribromide	5.6	
Aluminium trichloride	14.5		Vanadium chloride-oxychloride (1 : 1)	7.1	
Silicon tetrachloride	23.0	16.0	Chromium oxychloride	7.7	
Sulphur hexafluoride	195.0		Antimony pentachloride	6.1	
Sulphur chloride	10.6				
Thionyl chloride	15.1				
Nitro-halogen substituted hydrocarbons					
Tetranitromethane	88.0	38.5	Trichloronitromethane (chloropicrin)	15.5	12.0
Bromonitromethane	21.5		1,1-Dichloro-1-nitro-ethane	12.5	12.0
Monobromotrinitro-methane	15.7	17.0	1-Chloro-1-nitroethane	28.8	36.0
Dibromodinitromethane	11.4		2-Chloro-2-nitropropane	91.4	41.0
Tribromonitromethane (bromopicrin)	8.2	13.0			
Sulphur compounds					
Methyl disulphide	37.0		Methyl thiocyanate	115.0	
Ethyl sulphide	100.0		Methyl isothiocyanate	285.0	
n-Butyl mercaptan	108.0		*n*-Butyl thionitrite	130.0	
Carbon disulphide	205.0		Thionyl chloride	15.1	
Ethyl sulphide	100.0	143.0	Sulphur hexafluoride	195.0	
Benzene sulphonyl chloride	54.0		Sulphur chloride	10.5	
n-Propyl sulphone	132.0				
Miscellaneous					
Dichloromethylarsine	3.8	5.0	Ethyl orthosilicate	23.6	
Cacodyl chloride	4.2	5.0	Acetyl nitrate	140.0	
Lewisite		4.6	2-Nitrobutanol acetate	310.0	

Metal naphthenates

	Octane decrease at 0.3 gm./ 100 cc. fuel		Octane decrease at 0.3 gm./ 100 cc. fuel
Potassium naphthenate	(Insoluble)	Vanadium naphthenate	10.0
Copper naphthenate	2.3	Chromium naphthenate	4.2
Magnesium naphthenate	1.2	Manganese naphthenate	1.8
Zinc naphthenate	0.8	Iron naphthenate	3.0
Mercury naphthenate	16.0	Cobalt naphthenate	1.5
Lead naphthenate	0.8	Nickel naphthenate	3.3

Effect of Larger Concentrations of Pro-knock

Procedure

The procedure followed was similar to that previously employed except that where octane decreases of more than 10 units were obtained, a stepwise reduction in compression pressure was necessary for the various octane ranges. This is a valid procedure, since overlapping the ranges and plotting the results shows a smooth curve. Reference fuels were used to bracket each reading on the knockmeter in the lower ranges.

For this work an 80.5 octane aviation fuel was used, leaded to this value from a base stock of 64 octane units.

Results

The octane decreases resulting from various concentrations of pro-knocks are shown in Table II. Some of the results are illustrated further in the

TABLE II

OCTANE DECREASE OF LEADED AND UNLEADED NAPHTHA BY VARIOUS PRO-KNOCK AGENTS

(Octane rating of base stock 16.5 units less than that of leaded fuel)

Chloropicrin				Bromine				Arsenic trichloride		Phosphorus trichloride	
Leaded		Unleaded		Leaded		Unleaded		Leaded (unleaded—no effect)		Leaded (unleaded—no effect)	
Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.
6.0	6.0	30.0	5.0	14.0	16.0	20.0	1.0	3.5	10.0	4.5	11.0
15.5	15.0	42.0	6.5	20.0	17.5	41.5	3.0	6.0	14.0	12.0	14.0
25.0	19.5	58.0	7.5	25.0	19.0	70.0	3.5	12.0	16.5	16.7	15.7
82.0	29.5	79.0	10.0	45.0	19.5	85.0	4.5	24.0	17.0	35.0	17.0
90.0	31.0	97.0	12.0	80.0	21.0			64.0	17.0	65.0	17.7

Antimony pentachloride		Diphenyl-chloroarsine		Sulphuryl chloride		Bromo-picrin		Phosphorus oxychloride		Methyl *bis*-β-chloroethylamine	
Leaded (unleaded—no effect)		Leaded		Leaded		Leaded		Leaded		Leaded	
Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.
5.8	5.3	6.3	10.0	10.0	5.0	7.0	8.5	12.8	9.5	15.0	8.0
7.3	8.4	11.0	14.5	34.0	13.0	11.0	10.5	20.0	14.0	25.0	13.0
11.2	13.6	16.7	15.5	45.0	15.0	13.0	13.5	22.0	14.0	32.0	15.0
15.3	14.0	19.0	16.0	90.0	17.0	14.0	16.0	30.0	14.5	50.0	16.5
23.0	15.0	40.0	16.0			21.0	19.0			85.0	16.5

graphs in Fig. 2. The pro-knock activity of arsenic trichloride and phosphorus trichloride ceases to increase with concentrations greater than 14 p.p.m. This rather abrupt change of slope in the curve occurs at an octane

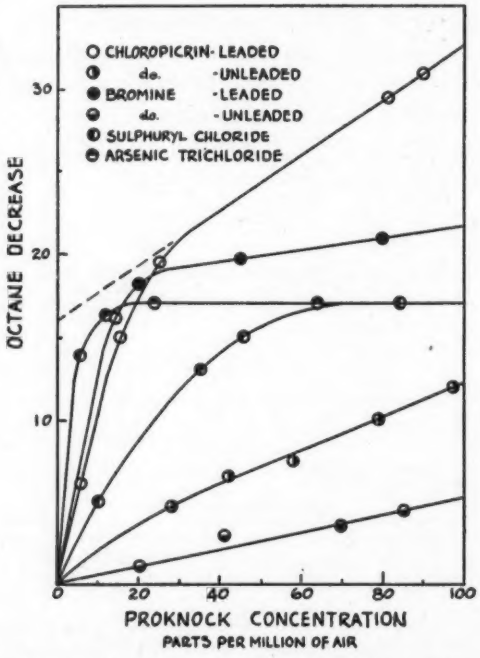


FIG. 2. *Effect of pro-knock concentration on octane number of gasolines containing no lead tetraethyl (octane number = 64) and containing lead tetraethyl (octane number = 80.5).*

decrease of about 16.5 units. Only large concentrations of phosphorus trichloride (of the order of 1000 p.p.m.) give any increase in knock with an unleaded fuel. Large concentrations of arsenic trichloride have no effect with an unleaded gasoline. Similar behavior is exhibited by diphenylchloroarsine, phosphorus oxychloride and methyl *bis*-β-chloroethylamine in decreasing order of effectiveness. Antimony pentachloride and thionyl chloride are somewhat similar except that the first attains a maximum about 1.5 units short of the others and falls off, while the second is very gradual. On the other hand, bromine, chloropicrin, and bromopicrin possess a different pro-knock characteristic. The change is more gradual and they have some influence on unleaded fuel. The straight line relation at high concentrations of chloropicrin for the leaded fuel parallels the relation between concentration and octane decrease for the unleaded fuel and extrapolates to a 16.5 octane decrease at zero concentration.

From these considerations it is evident that the effect of certain of the pro-knock compounds is primarily to overcome the effect of lead tetraethyl on the fuel. Thus it becomes apparent that the octane decrease produced by the pro-knock depends, to a large extent at least, on the difference between the octane rating of the base fuel and that of the leaded gasoline.

Aside from this conclusion there are other interesting points. With antimony pentachloride the equilibrium

$$SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$$

could be rapidly shifted to the right under operating conditions. It is probable that antimony in both the penta- and trivalent forms is capable of overcoming the effect of the lead tetraethyl, but trivalent antimony is the more stable form and possesses good antiknock properties (18) which are observed at the higher concentrations of the adulterant.

Diphenylchloroarsine possesses about the same activity as arsenic trichloride which demonstrates the specific action of the arsenic atom in compensating the influence of added lead tetraethyl.

The relation between the octane decrease produced by the pro-knock and the difference in octane ratings of the base and leaded fuels was studied in more detail by determining the effect of arsenic trichloride and chloropicrin on a graduated series of leaded gasolines.

Shell naphtha, an aviation base of 64 octane, was used. Portions were leaded with 0.25, 1.0, 2.0, and 4.0 cc. of lead tetraethyl per U.S. gallon. Octane ratings were determined on the engine to its maximum range and thereafter from a lead susceptibility chart (20, p. 2937) kindly supplied by the Shell Oil Company. Various concentrations of pro-knock were added and the octane drop determined.

The results are plotted in Fig. 3. With arsenic trichloride a family of curves is obtained, each curve sloping off at the octane rating of the base fuel. Further increases in concentration of the pro-knock have no effect. The concentration of arsenic trichloride at the point of intersection represents complete counteraction of the effect of the lead added. Comparison with the concentrations of lead tetraethyl, and with the antiknock effect produced by the lead tetraethyl, gives the following ratios:

Arsenic trichloride concentration	1 : 2.1 : 3.2 : 4.0
Lead tetraethyl concentration	1 : 4 : 8 : 16
Antiknock effect of lead tetraethyl	1 : 2.5 : 3.4 : 4.0

This would indicate that such pro-knocks counteract the antiknock effect of the lead tetraethyl rather than the tetraethyl itself.

For arsenic trichloride and for lower concentrations of phosphorus trichloride a straight line relation exists between the maximum octane change and the volume per cent pro-knock just sufficient to produce this change. Also

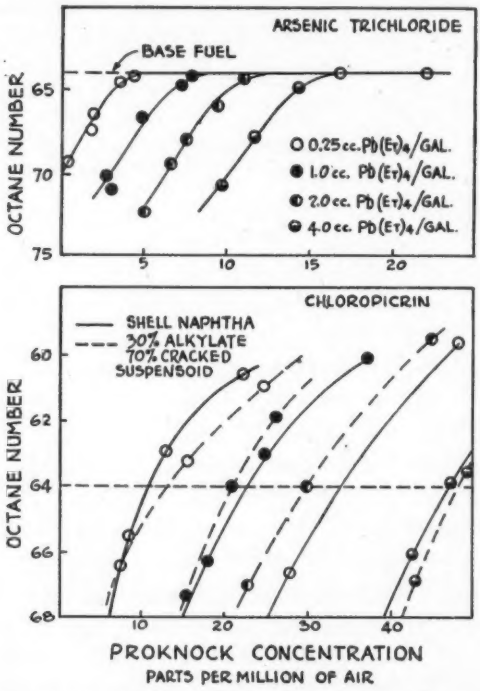


FIG. 3. *Relation of pro-knock concentration to octane number decrease for leaded and base stocks (legends common to both graphs).*

illustrated (Fig. 4) is the relation between the concentration of lead tetraethyl and the concentration of pro-knock to neutralize the octane improvement resulting from the lead tetraethyl. The molar relations are shown in Fig. 5 and in addition a curve to show the relative atomic effects of lead and arsenic. It is obvious that the action of pro-knock compounds such as arsenic trichloride and phosphorus trichloride is a neutralization of the antiknock effect of the lead tetraethyl and not a neutralization of the lead tetraethyl itself.

The action of chloropicrin, which has some pro-knock effect on the base fuel, was also studied in greater detail. The family of curves obtained (Fig. 3) when the octane decrease is plotted against the concentration of chloropicrin does not show the falling-off at the octane rating of the base stock, but rather the pro-knock effect continues without a break in the curve. The intersections were treated similarly to those of the arsenic trichloride curves, in Figs. 4 and 5.

The molar relation between pro-knock and antiknock concentration for chloropicrin is a straight line, unlike that of arsenic trichloride, which falls off rapidly at higher lead contents.

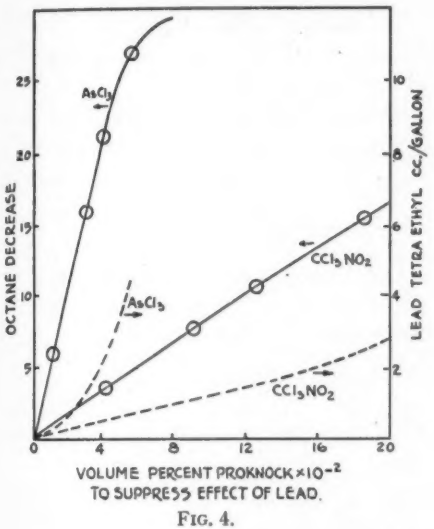


FIG. 4.

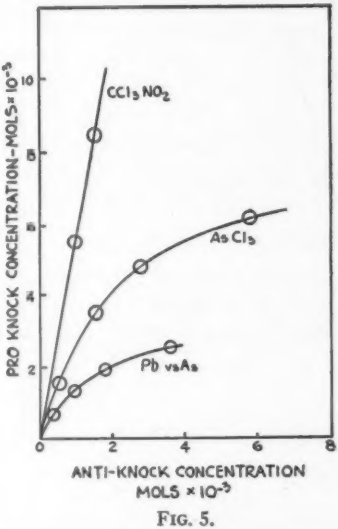


FIG. 5.

FIG. 4. *Relation between concentration of pro-knock to suppress the effect of lead tetraethyl, and (a) the decrease in octane number corresponding to the suppression, (b) the lead tetraethyl content of the gasoline.*

FIG. 5. *Molar relations between antiknock concentration and concentration of pro-knock to suppress the effect of the antiknock.*

These results were obtained using Shell naphtha base fuel. Similar curves were obtained for a gasoline of 70% cracked suspensoid and 30% alkylate.

Effect of Composition of Base Stock

Since automotive fuels are made up from gasolines of various chemical compositions, a study was made of the effects of pro-knock concentration and lead content for fuels of various typical base stocks. It is well established that the octane increase obtained using lead tetraethyl varies considerably with the base stock. A measure of this difference in the response of gasolines to lead tetraethyl is the lead susceptibility of the gasoline, i.e., the increase in octane rating per cubic centimeter of lead tetraethyl added (19). This lead response for different fuels increases in the following order: cracked, straight run, and natural gasolines and isopentane. The lead susceptibility for any gasoline decreases as its octane number is raised, but possibly this is due to the knock testing standards. An increase from 80 to 85 octane units indicates relatively greater improvement in engine performance than from 50 to 60 units.

From this it might be expected that the greatest octane decrease possible would be in a gasoline of high lead susceptibility, leaded from a low octane base stock. Similar experiments to those described in the previous section but using gasolines of base stocks of various compositions show the maximum octane drops possible through use of pro-knock compounds and the concentrations required.

Procedure

A series of fuels was made up by adding increasing proportions of benzene to Shell naphtha, a base stock of 64 octane units. Each of these was treated with various amounts of lead tetraethyl. Arsenic trichloride was used as the adulterant in these experiments.

Results

In Fig. 6 are graphs showing the octane number decrease corresponding to complete neutralization of the lead tetraethyl as a function of the pro-knock concentration necessary to cause this decrease.

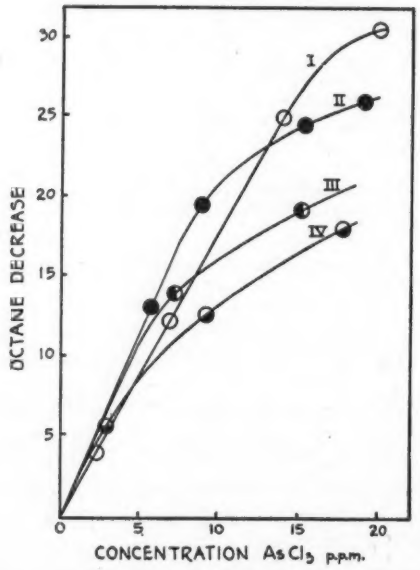


FIG. 6. *Effect on pro-knock activity of decreasing the lead susceptibility and increasing the octane number of the base fuel with benzene.*

N = *Octane number*
S = *Lead susceptibility*

I $N = 64\ S = 3.0$ (*Shell naphtha*)
II $N = 67\ S = 2.5$ (*Shell naphtha + 15% benzene*)
III $N = 69\ S = 2.3$ (*Shell naphtha + 25% benzene*)
IV $N = 75\ S = 1.8$ (*Shell naphtha + 40% benzene*)

As the concentration of benzene is increased, the octane rating of the base stock increases as its lead susceptibility is decreased. This appears to make it easier for the pro-knock to effect a given octane decrease in the initial stages. Similar results were obtained using alkylate in place of benzene in the base stock. The results illustrate that the important characteristics of a fuel in relation to the ease with which a pro-knock could effect a decrease in octane rating is not so much the composition of the fuel but the inherent values of lead susceptibility and base octane number.

The relative importance of base octane number and lead susceptibility was investigated further. In Fig. 7 the effect of the lead susceptibility of a

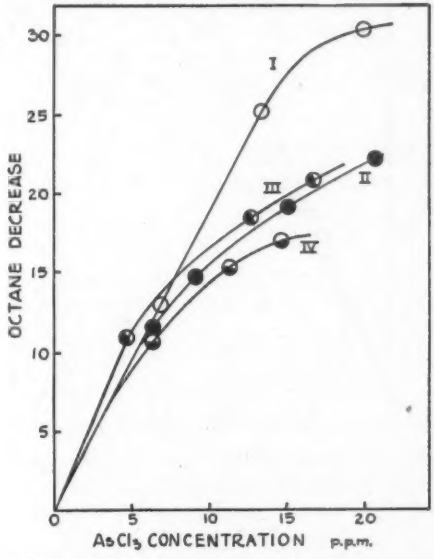


FIG. 7. *Relation of pro-knock concentration to octane number decrease for gasolines of different lead susceptibilities but the same octane rating.*

N = *Octane number*
S = *Lead susceptiblity*

I $N = 64\ S = 3.0$ (*Shell naphtha*)
II $N = 64\ S = 2.3$ (*40% benzene + 60% straight run*)
III $N = 69\ S = 2.3$ (*25% benzene + 75% Shell naphtha*)
IV $N = 69\ S = 1.2$ (*40% benzene + 60% suspensoid*)

fuel at constant octane rating is illustrated. At high lead susceptibility a large drop in octane rating is caused by a relatively small arsenic trichloride concentration completely nullifying the effects of the lead tetraethyl. This effect decreases as the lead susceptibility decreases. In a 64 octane base stock the reduction in octane change as between fuels of lead susceptibility of 3.0 and

2.3 (Curves I and II) is much greater than the corresponding reduction as between fuels of lead susceptibility of 2.3 and 1.2 in a 69 octane base stock (Curves III and IV).

The effect of the octane rating of the base stock is illustrated in Fig. 8, in fuels of similar lead susceptibility. Curves III and IV show the effect of wide variation in octane rating of the base stock. Curve III shows that for blends

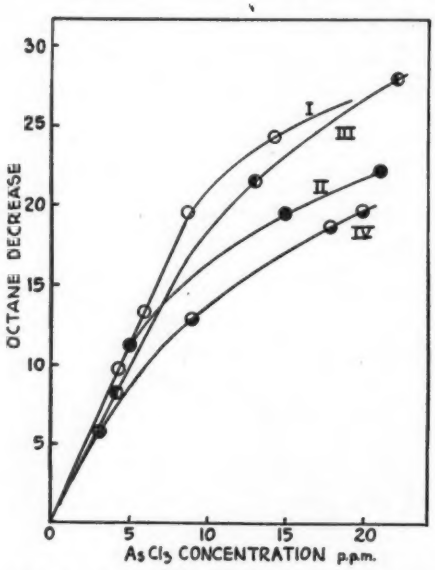


FIG. 8. *Relation of pro-knock concentration to octane number decrease for gasolines of different octane ratings but the same lead susceptibility.*

N = *Octane number*
S = *Lead susceptibility*

I $N = 67$ $S = 2.5$ (*Shell naphtha + 15% benzene*)
II $N = 80$ $S = 2.6$ (*Shell Reference Fuel*)
III $N = 49$ $S = 1.8$ (*Heavy straight run*)
IV $N = 75$ $S = 1.8$ (*Shell naphtha + 40% benzene*)

of low base octane number whatever increase is effected by the lead tetraethyl is readily nullified by pro-knock. Thus it would appear that in general the activity of a pro-knock specific for counteracting lead is decreased with increase in the base octane number of the fuel.

Counteraction of Various Antiknock Compounds

Tests made to observe the activity of pro-knocks in fuels whose octane ratings had been increased by antiknock agents other than lead tetraethyl show similar results, as illustrated by the curves in Fig. 9.

Chloropicrin is effective in counteracting nickel carbonyl (I) in concentrations similar to those required to counteract lead tetraethyl, but bromine requires considerably larger concentrations (III). The octane drop effected

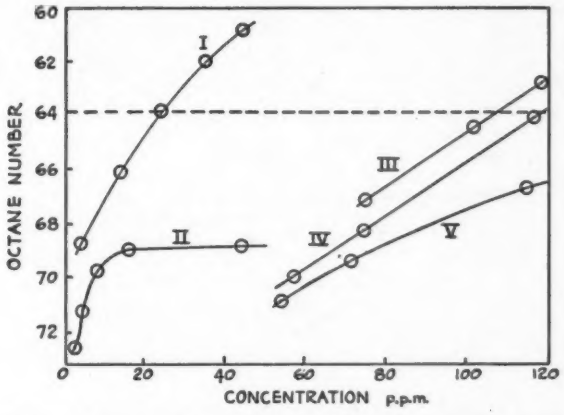


FIG. 9. *Relation between pro-knock concentration and octane number decrease with gasolines containing antiknock agents other than lead tetraethyl.*

I Chloropicrin (pro-knock) – nickel carbonyl (antiknock)
II Arsenic trichloride (pro-knock) – nickel carbonyl (antiknock)
III Bromine (pro-knock) – nickel carbonyl (antiknock)
IV Chloropicrin (pro-knock) – aniline (antiknock)
V Bromine (pro-knock) – aniline (antiknock)

by arsenic trichloride falls off rapidly with increasing concentrations of the pro-knock and reaches a maximum within five octane units of the base stock. Apparently the action of this antiknock cannot be completely counteracted by arsenic trichloride.

Chloropicrin and bromine also effectively counteract the antiknock effect of aniline (IV and V), whereas arsenic trichloride has no effect. Presumably this is due to a difference in antiknock action and indicates that organometallic pro-knocks cannot affect organic antiknocks.

The molar relations between the equivalent concentrations of pro- and antiknock compounds are shown in Fig. 10, for counteraction of both lead tetraethyl and iron carbonyl by arsenic trichloride. Arsenic trichloride is just as efficient in counteracting iron carbonyl as lead tetraethyl. Here again the arsenic trichloride concentration is related to the octane change brought about by the carbonyl and not necessarily to the amount present. The action of lead tetraethyl and iron carbonyl would thus appear to be the same, although it requires five times as much iron carbonyl in this particular fuel. The fact that the counteraction of lead tetraethyl and iron carbonyl by arsenic tri-

chloride may be illustrated by a single curve indicates that the mechanism of increasing and decreasing the octane rating is identical.

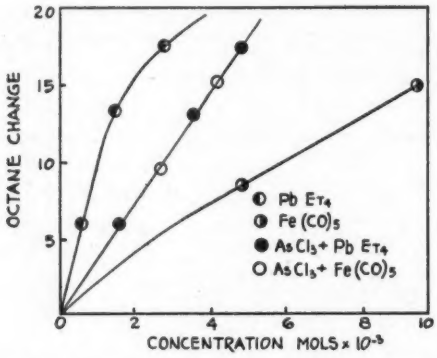


FIG. 10. *Molar relations of anti- and pro-knock agents in Shell naphtha.*

Miscellaneous Effects

Tests on the pro-knock activity of arsenic trichloride on dried and undried fuels indicate a slight impairment by the moisture present. With lewisite the hydrolysis had little effect.

The effect of engine temperature on the action of various pro-knock substances is not appreciable. The action of arsenic trichloride is reduced slightly at the higher concentrations of lead tetraethyl. Chloropicrin shows greater susceptibility to temperature change than bromine or arsenic trichloride. It is slightly more effective at lower jacket temperatures. This might be true in general for organic pro-knocks since they would be more rapidly decomposed at higher temperature.

The effect of octane decrease on the power developed was studied, using a recording wattmeter. An octane decrease of 10 units causes about a 5% decrease in the power developed by the engine. The power loss caused by the octane decrease due to pro-knock action is the same as that caused by the use of a correspondingly poorer fuel.

Several pro-knock substances such as amyl thionitrate and chloropicrin are known to improve the combustion characteristics of Diesel fuels. The results of some experiments on the effect of chloropicrin and diphenylchloroarsine are shown in Table III.

It may be seen that pro-knock compounds specific for counteracting lead tetraethyl are useless for the improvement of Diesel fuels. It is possible that bromopicrin, which is a better pro-knock compound than chloropicrin, would show correspondingly greater improvement in the Diesel fuel.

TABLE III

Fuel	Cetene number
Base Diesel fuel	44
Base plus chloropicrin, 1.62 gm./liter	48
" " " 5.2 "	52
" " diphenylchloroarsine, 1.25 gm./liter	44
" " " 3.75 "	43

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THE OXIDATION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

V. THE HYDROGEN ENGINE AND THE NUCLEAR THEORY OF IGNITION[1]

By R. O. King,[2] W. A. Wallace,[3] B. Mahapatra[4]

Abstract

It should not be possible, according to the nuclear theory of ignition, stated in Part IV, to obtain ignition in the body of a gaseous combustible mixture by any method of heating if it remain truly homogeneous while the temperature is raised. Such mixtures cease to be homogeneous when heated by sudden compression to the temperatures required for ignition because of the formation of finely divided carbon by pyrolysis of lubricating oil or of hydrocarbon vapor. The finely divided carbon provides nuclear centers of ignition in the gaseous mixture. Ignition due to finely divided carbon produced by pyrolysis of the lubricant is demonstrated by experiments with hydrogen as the fuel for a C.F.R. engine. The usual pre-ignition and severe knocking were obtained when the engine in normal condition was run on hydrogen, and it was impossible, as previously found by others, to use any but weak mixtures even at low compression ratios. When however the combustion space was decarbonized and thereafter maintained reasonably clear of fluffy carbon, hydrogen could be used as the sole fuel at any compression ratio up to the limit of 10 : 1 possible with the engine, and at any mixture strength ranging from very weak to very rich, while power output varied accordingly. Conversely pre-ignition and combustion knock reappeared when carbon dust was admitted with the combustible mixture.

Introduction

Hydrogen–air mixtures when used in an Otto cycle engine are heated by sudden compression and by contact with hot surfaces such as exhaust valves. The tendency of the mixture to 'detonate' or to explode prematurely in the usual conditions of operation limits the power and efficiency to relatively low values. Ricardo (12), using the E35 engine, cylinder diameter 4.5 in., found that if the mixture with air contained 50% only of the hydrogen required for combining proportions, a compression ratio of 7 : 1 could be used and the high thermal efficiency of 37.5% obtained. It was necessary to lower the compression ratio progressively as the hydrogen concentration was increased but even so it was not possible to use the mixture strength for maximum power. "If an attempt were made to run with a rich hydrogen–air mixture, violent pre-ignition occurred, accompanied by firing back in the carburetor, which rendered further running impossible. Even with the compression ratio lowered to 3.8 : 1 the same thing occurred". There seemed to be a limiting indicated mean effective pressure (I.M.E.P.) of 74 lb. per sq. in. Attempts to obtain higher values by increasing hydrogen concentration or by raising

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the compression ratio were always defeated by the onset of detonation or pre-ignition. The range of mixture strength usable with various engine fuels was discussed by Ricardo in a later publication (13, pp. 42–43) and, in respect of hydrogen, it was stated that "the range of burning could not be explored because, so soon as any excess of hydrogen was admitted, back firing occurred through the inlet valves". Ricardo's conclusions were confirmed by A. F. Burstall (1) even in respect of the I.M.E.P. having a limiting value of approximately 74 lb. per sq. in. The experiments of Egerton, Smith and Ubbelohde (4) with hydrogen as fuel for a Delco knock testing engine, cylinder diameter 2.5 in. only, demonstrated that knocking combustion was not restricted to engines having relatively large cylinders. Egerton (4, p. 517) attributed the detonation to nitrogen peroxide formed from the nitrogen of the air.

The combustion phenomena described by Ricardo and others are usually attributed to ignition of the hydrogen–air mixture by hot surfaces or to ignition being the final result of a chain reaction proceeding at the temperature attained by sudden compression. An alternative explanation is afforded by the nuclear theory of self ignition advanced in Part IV (10), the finely divided carbon for nuclear centers of ignition, as required by the theory, being provided by pyrolysis of the lubricating oil. Experiments made accordingly in the Heat Engine Laboratory of the University of Toronto and described in Section I show that hydrogen can be used as the fuel for an Otto cycle engine, in any mixture proportion with air and at compression ratios rising to 10 : 1, without pre-ignition or detonation if the concentration of finely divided carbon in the gaseous mixture be maintained at a relatively low value.

Section I

Experimental

The Co-operative Fuel Research Committee (C.F.R.) knock testing engine was used for the experiments with hydrogen. The bore is 3.25 in. and the stroke 4.5 in. The compression ratio can be varied from 4 to 10 : 1. The cylinder is maintained normally at a nearly constant temperature of 212° F. by the evaporation of distilled water at atmospheric pressure. The engine is connected to a d-c. main generator and to a similar auxiliary generator. Speed is controlled manually by adjusting the field excitation of the main generator and the electrical output absorbed by a resistor bank.

Lubrication.—The piston is fitted with three pressure rings and one oil scraper ring. A partial vacuum is created in the crank case by fitting the breather with a nonreturn flap valve that closes during the compression and exhaust strokes. The rate of oil consumption in the circumstances is so low that, after 100 hr. running, careful measurement is required to determine the quantity used. The oil in the crank case was maintained at a temperature of between 120° and 130° F. by a manually controlled electric heater. A commercial brand of S.A.E. 30, without 'additives', was used during the experiments.

Hydrogen Supply.—The standard horizontal carburetor with 9/16 in. diameter venturi and no throttle plate was used for the experiments. Hydrogen was admitted to the throat of the venturi through a 0.125 in. diameter hole in a screw which replaced the standard hold down screw of the unused cap jet. Hydrogen procured by electrolysis was supplied in the usual pressure bottles by the Dominion Oxygen Company, and contained not more than 0.3% of oxygen. The hydrogen passed through an adjustable pressure reducing valve, then through a fine adjustment needle valve to a circular square edged metering orifice in a thin plate and thence to the carburetor venturi. The rate of supply to the engine was taken to be proportional to the square root of the pressure difference, in inches of water, across the orifice.

Air Supply.—Air was taken in by the engine at laboratory temperature and the humidity not controlled. The standard air inlet to the carburetor comprises a short piece of 1¼ in. I.D. tubing ending in a 90° elbow into which is fitted a long inlet pipe (20½ in.) also 1¼ in. diam. Eight inches of the outer end is arranged as a silencer but the diameter of the tube is not reduced. The standard pipe inlet was on occasion replaced by a swirl chamber 6 in. diam. and 6½ in. long provided with tangential inlets and outlets. The cover of one end was a 'push on' fit and blew off when back firing through the carburetor (induction ignition) occurred.

The Inlet Valve.—The standard inlet valve is fitted with a 180° shroud so arranged that the combustible mixture is given a swirling motion on entering the cylinder. The arrangement has been found of beneficial effect in respect of determinations of the relative antiknock values of gasolines, but it reduces volumetric efficiency and is not used in practice.

Definition of the Terms Used to Describe Abnormal Ignition or Combustion

Detonation knock describes an effect due to the self-ignition and explosion of the gas ahead of the flame (end gas). Eliminating the knock by retarding ignition gives rise to a *decrease* of power.

Combustion knock describes an effect due to an abnormally high rate of flame propagation. The knocking sound in the C.F.R. engine is similar to that heard when detonation occurs. Eliminating or reducing the knock by retarding ignition gives rise to an *increase* of power. This characteristic makes it possible to distinguish between combustion knock and detonation knock.

Induction ignition describes the effect obtained when the combustible mixture ignites before the inlet valve closes. The effect gives rise to explosions in the induction system and carburetor, the violence depending on mixture proportion and the volume involved. The explosions occur irregularly.

Pre-ignition is initiation of combustion after the inlet valve closes and before ignition by spark. If the ignition occurs sufficiently late in the compression stroke, the engine will run without spark ignition but generally at reduced power and for relatively short periods of time.

Preliminary Engine Experiments with Unclean Combustion Chamber

The experiments were begun with the engine as found. It had been run for some weeks on hydrocarbon fuels, generally leaded. The compression ratio was set at 5 : 1, the ignition timing at 30° advance, and the engine run at 900 r.p.m. for a warming up period of one hour on leaded gasoline. The gasoline was then shut off* and hydrogen admitted at a sufficient rate to maintain the engine speed of 900 r.p.m., with light load. On increasing the rate of hydrogen supply and the load, severe knocking occurred, accompanied by occasional induction ignition. Thus the characteristics of hydrogen combustion in an engine as observed by Ricardo, Burstall, and Egerton had been recovered.

Very rich mixtures were then admitted. Combustion was silent and without induction ignition, just as when very weak mixtures were used. This interesting characteristic seems to have been overlooked by earlier experimenters.

It was observed during the experiments mentioned that knock always decreased on retarding ignition, while power increased; this indicated combustion knock rather than detonation knock.

The engine was dismantled for observation of the condition of the combustion chamber surfaces. The piston crown was found to be thickly coated with hard carbon. The piston ring grooves contained granular carbon but the rings were free. The exhaust valve was coated with a greyish white deposit. The inlet valve was fairly clean. The surfaces were thoroughly cleaned and the shrouded inlet valve replaced by a spare exhaust valve of the common tulip shaped type.

First Set of Trials with the Engine Combustion Space Initially Clean. Jacket Temperature, 212° F.; Compression Ratios Rising to 10 : 1, and Arbitrarily Chosen Ignition Timing

Preliminary trials were carried out after warming up the engine by running on leaded gasoline before changing over to hydrogen. There was then no induction ignition at any compression ratio within the range of the engine. Combustion was silent at compression ratios up to 8 : 1 but slight combustion knock occurred at 10 : 1 when using the mixture strength for maximum power. It developed later that ignition had been set too far advanced.

A complete set of trials was then carried out at compression ratios of 4.2, 6.0, 8.0, and 10 : 1 and with the hydrogen–air mixtures varying from very weak to very rich. It was supposed, judging from experiments made by others, that a considerable spark advance would be required for weak mixtures used at low compression ratios and less advance on increasing mixture strength and compression ratio, but nothing definite was known because previously it had not been possible to use anything but weak mixtures at any compression ratio. Trial spark settings of 30°, 20°, 10°, and 0° for the compression ratios mentioned were therefore used.

* *The engine was warmed up by running on gasoline in order to save hydrogen.*

The experimental results are given by the graphs of Fig. 1; net power output in kilowatts being plotted against rate of hydrogen supply. The values for rate of hydrogen supply are the square roots of pressure differences in inches

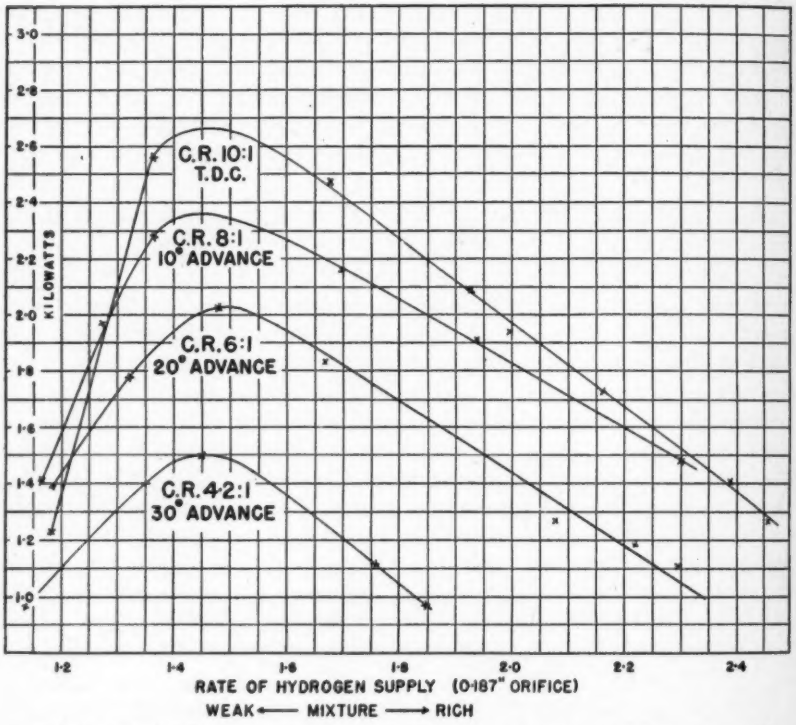

FIG. 1. *Relation between power output and mixture strength at compression ratios rising to 10 : 1. Jacket temperature, 212° F.*

of water across a circular square edged metering orifice, 0.187 in. diameter, in a thin plate. The graphs are of interest in showing for the first time on record that it is possible to run an engine on hydrogen in any proportion in a mixture with air at compression ratios rising to 10 : 1 and without any combustion difficulty as is evidenced by the consistent variations of power with changes of compression ratio and mixture strength.

Sundry Experiments and Recurrence of Induction Ignition and Knock

Air oscillation in the induction system of the C.F.R. engine is considerable and it appeared that some of the hydrogen supplied at the carburetor throat might accordingly be carried out of the standard inlet pipe to escape into the atmosphere. The standard pipe was therefore replaced by the swirl chamber.

The 0.187 in. diam. orifice for metering the hydrogen was replaced by one of 0.125 in. diam. in order to obtain greater and more easily readable pressure differences, and for further convenience of reading pressure differences the U-tube type of manometer was replaced by one of the single leg variety.

Experiments with hydrogen were resumed on completion of the changes mentioned, after the usual warming up of the engine by running for an hour on leaded gasoline. The earlier combustion difficulties were again encountered and it was impossible to run with the 'correct' mixture strength, even at the low compression ratio of 4 : 1, without violent explosions in the induction system. The difficulties were not overcome by replacing the swirl chamber by the standard inlet pipe, by warming up the engine on unleaded gasoline, or by approaching 'correct' mixture strength from the rich instead of the weak side, or by lowering or raising the jacket temperature, or by taking precautions to avoid electric charges in the induction system possibly due to the high velocity of the mixture passing over sharp edges.

The time of running since the first cleaning was about 12 hr. and the engine was dismantled for inspection of the combustion space and the valves. Both valves were found to have been seating properly and were clean. The exhaust valve showed oxidation colors, brown and red. The piston rings were free but there was some loose carbon in the grooves. The water cooled surfaces were free of loose carbon. The significant finding was a layer of *fluffy carbon*, having the appearance of lamp black, on the piston crown. The combustion chamber, the inlet passageways, and the ring grooves were thoroughly cleaned and the engine reassembled for further trials.

Second Set of Trials, Combustion Space again Initially Clean. Jacket Temperature, 212° F. Air Supply Through Swirl Chamber with Cover Off

The trials were made primarily to verify that the recurrence of combustion difficulties was due to the fluffy carbon mentioned above. They were run at compression ratios of 6, 8, and 10 : 1 and spark setting varied to determine optimum values in varying conditions of mixture strength and compression ratio. There was not a single case of induction ignition in the whole set of trials; combustion was notably quiet except when using the mixture strength for maximum power at a compression ratio of 10 : 1. There was then slight combustion knock.

The experimental results are given by the three sets of graphs of Fig. 2. It is of special interest that maximum power for any but the weakest or richest mixture was obtained when ignition occurred at or very near top dead center. At 10 : 1 compression ratio maximum power was obtained with the spark 5° *retarded*. Regular ignition at this high compression ratio was obtained by reducing the spark gap from the standard setting of 0.025 in. to 0.013 in. Maximum power at 8 : 1 compression ratio was obtained with a spark advance of 5°, whereas at the lower compression ratio of 6 : 1, the optimum setting was at 0°, a somewhat inconsistent result justifying a repetition of the experiments.

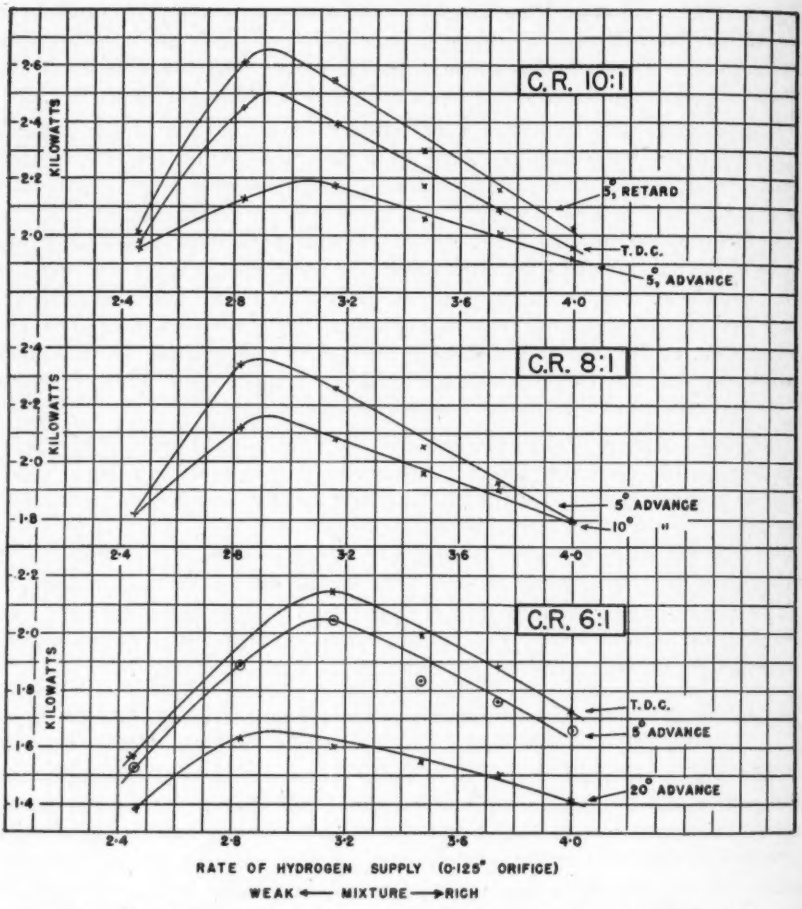

FIG. 2. *The effect of ignition timing on power output at compression ratios rising to 10 : 1. Jacket temperature, 212° F.*

Routine Cleaning Method

The experiments described above occupied about two hours' running time and no doubt the usual combustion difficulties would have recurred on continued running if no precaution had been taken to maintain the combustion space reasonably clear of fluffy carbon. A routine cleaning method was therefore adopted. Thus, always before starting a day's experiments the bouncing pin and spark plug were removed, the piston moved to top dead center, and the crown cleaned with a tooth brush inserted through the spark plug hole. The engine was then motored round to blow loose carbon through the holes mentioned. As a further precaution to avoid carbon formation by

pyrolysis of hydrocarbon fuel the warming up period on gasoline was reduced to the time required to heat the jacket water to the boiling point and any further warming up done with hydrogen.

The engine was used after the adoption of the cleaning routine for a complete set of trials at low jacket temperature, extended trials using town gas and some sundry experiments made in preparation for future experimental work. There was no recurrence of combustion difficulties.

Third Set of Trials, Routine Cleaning of Combustion Space. Jacket Temperature, 95° to 100° F.

The experiments so far described were made with the standard C.F.R. method of evaporative cooling of the water jackets, that is, jacket water temperature was always 212° F. It is not customary to use such high temperatures in practice and as a matter of interest a set of trials was made with the jackets cooled by tap water, the flow being regulated to maintain an outlet temperature of 95° to 100° F. The standard C.F.R. air inlet pipe was used because it was found during the sundry trials mentioned above that slightly more power was obtained than when using the swirl chamber inlet, no doubt because of the ramming effect of the pipe.

The optimum spark setting for compression ratios of 4, 6, 8, and 10 : 1 was determined for varying mixture strengths. It was found that the optimum setting for the maximum power mixture strength was also the optimum for any richer mixture. But for mixtures on the weak side there would be some advantage in advancing the ignition progressively in accordance with the diminution of hydrogen concentration in the mixture with air.

The trials were made when using the optimum spark setting for the maximum power mixture strength. The experimental results are given by the graphs of Fig. 3. The running of the engine was exceptionally smooth and quiet even when using the mixture strength for maximum power at a compression ratio of 10 : 1.

It will be noted that the graphs are nearly parallel on the rich mixture side but not on the weak side, as would be expected from the finding that the optimum spark advance for the maximum power mixture was also the optimum for richer but not for weaker mixtures.

The Effect of Carbon Nuclei Added to the Hydrogen–Air Mixture

It has been demonstrated by the experiments so far described that induction ignition and combustion knock in the hydrogen engine are due to the igniting action of carbon nuclei derived from the pyrolysis of the lubricating oil. It became of interest, therefore, to observe the effect of carbon nuclei added to the entering gaseous mixture.

The carbon used for the experiments was pulverized charcoal screened with a 200 mesh sieve. It was described as having been activated by heating but had been standing open to the laboratory atmosphere for some weeks before

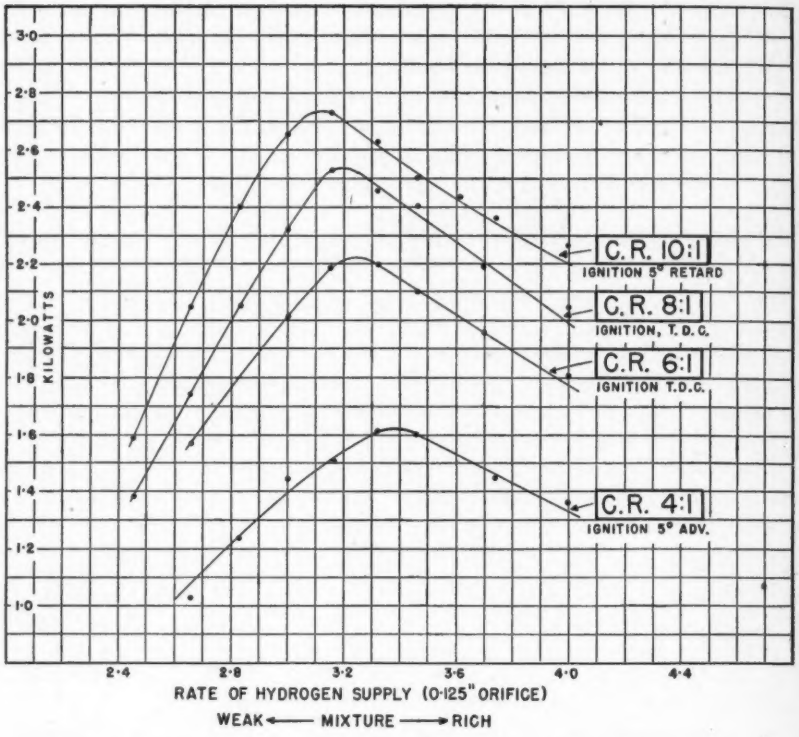

FIG. 3. *Relation between power output and mixture strength at compression ratios rising to 10 : 1, nearly optimum ignition timing. Jacket temperature, 95 to 100° F.*

being used for the experiments. The carbon was admitted to the air stream in advance of the carburetor throat, at a measured rate, by a device similar to a screw feed coal stoker. The experiment was begun with the combustion space in the condition maintained by the routine cleaning method. The standard pipe inlet was fitted and the jacket water maintained at 212° F. by the standard method.

The engine was started on hydrogen and run at a compression ratio of 6 : 1, with the mixture strength for maximum power and ignition at top dead center. There was no induction ignition, and combustion was silent. The carbon was then admitted at a rate of approximately 2.0 mgm. per stroke. Combustion knock occurred almost immediately and was followed by induction ignition accompanied by explosions in the induction system.

Preparations had been made to carry out a series of experiments to measure the rate of carbon supply required to induce premature ignition and combustion knock or detonation at compression ratios rising to 10 : 1, but, perhaps

as should have been expected, the carbon dust accumulated in the engine to such an extent that induction ignition and combustion knock continued when the supply of carbon to the induction system was shut off.

Indicated Mean Effective Pressure and Indicated Thermal Efficiency

The experiments with the hydrogen engine are regarded as confirming the nuclear theory of ignition. It is of importance, nevertheless, to show that confirmation was obtained while values of the indicated mean effective pressure (I.M.E.P.) and indicated thermal efficiency were such as would be expected from the compression ratios and mixture strengths used during the experiments.

The indicated power was determined by the motoring method. That is, the power required to motor the engine at the experimental speed of 900 r.p.m. was measured immediately after cutting off the fuel supply and added to the net power output measured previously. The method has been widely used by Ricardo and others, and, although it involves the unwarranted assumption that engine friction is of the fluid variety and therefore independent of load, values obtained accordingly are useful for purposes of comparison.

I.M.E.P.—The power required to motor the engine at 900 r.p.m., jacket temperature 212° F., was determined after warming up, using benzene as the fuel, at compression ratios of 6, 8, and 10 : 1. The piston area is 8.28 sq. in., stroke 0.375 ft., and at 900 r.p.m.—

$$\text{I.M.E.P. (lb. per sq. in.)} = \text{Indicated horse power} \times 23.6.$$

Maximum power output being taken from the graphs of Fig. 2, the data given in Table I are obtained.

TABLE I

INDICATED MEAN EFFECTIVE PRESSURES AT COMPRESSION RATIOS OF 6, 8, AND 10 : 1, WHEN USING THE MAXIMUM POWER MIXTURE STRENGTH

Compression ratio	Net output, kw.	Motoring power, kw.	I.H.P.	I.M.E.P., lb./sq. in.
10 : 1	2.66	1.61	5.73	136
8 : 1	2.36	1.59	5.30	125
6 : 1	2.15	1.48	4.87	103

Indicated Thermal Efficiency.—Relative rates of hydrogen supply are reasonably accurate but approximate values only of quantities were obtained, the metering orifice not having been calibrated. Thermal efficiencies calculated accordingly, again using data from Fig. 2, are given in Table II.

TABLE II

INDICATED THERMAL EFFICIENCIES; COMPRESSION RATIO, 10 : 1

Mixture strength	Net power, kw.	Indicated power, kw.	I.H.P.	Indicated thermal efficiency, %
15% rich	2.40	4.01	5.38	34.2
3% rich	2.64	4.25	5.70	39.8
Max. power	2.66	4.27	5.78	41.2
5% weak	2.58	4.19	5.62	42.4
17% weak	2.02	3.63	4.87	42.0

It will be noted from Table II that maximum efficiency was obtained for the mixture strength giving somewhat less than maximum power, as would be expected.

Section II

Discussion of Experimental Results

Induction ignition, normally described as "firing back through the carburetor", was obtained when, starting with a clean engine, sufficient time elapsed for an accumulation of fluffy carbon in the combustion space. The effect was not obtained if accumulation of the carbon were prevented. It is concluded that ignition of the fresh charge when obtained was due to glowing particles of carbon present in the residual charge.

Ignition by sudden compression.—The absence of the effect when the engine combustion space was nearly free of fluffy carbon is of interest in respect of experiments by others on the ignition of electrolytic gas ($2H_2 + O_2$) and hydrogen–air mixtures by sudden compression. Falk (5,6) concluded that the presence of lubricant (lanoline) was without effect on ignition temperature, but the experiments of Dixon, Bradshaw, and Campbell (2) and Dixon and Crofts (3) demonstrated that consistent ignition temperatures could be obtained solely when the lubricant was present as an extremely thin film on the surface of the combustion space, a condition set by the vacuum method of filling the space with the combustible mixture. Tizard (14), using the Ricardo compression ignition machine, similar to an engine cylinder, could not avoid the presence of a thin film of lubricant on surfaces exposed to the temperatures of compression and obtained ignition temperatures accordingly. When the Ricardo machine was redesigned to permit compression of the combustible mixture in a cylinder supposed to be free of lubricant, Tizard and Pye (15) were unable to obtain consistent ignition temperatures. Fenning (8), on continuing experiments with the machine, found that lubricant did in fact penetrate into the compression cylinder in an irregular manner. Thus, out of five compressions with a compression ratio of 9.2 : 1 and a jacket temperature of 97° C., two compressions resulted in premature ignition, two caused ignition after delay periods of 0.009 and 0.015 sec. and a fifth failed to cause ignition.

Nevertheless, when using the hydrogen engine at 10 : 1 compression ratio, a jacket temperature of 100° C. and more nearly adiabatic compression, the mixture failed to ignite prior to passage of the spark, if the combustion space were nearly free of finely divided carbon. That is, ignition did not occur in the body of the gaseous mixture in the absence of material nuclei of ignition as would be expected from the experiments of King (9) and King and Mole (11).

Flame velocity.—It is generally agreed that maximum engine power is obtained when maximum combustion pressure occurs about 12° after top dead center. It will be seen from Figs. 2 and 3 that at 10 : 1 compression ratio maximum power was obtained when the spark passed at 5° after top dead center. Combustion was thus completed in about 7° of crank angle, that is in 0.0013 sec., engine speed being 900 r.p.m. The flame would have traveled a distance equal to the diameter of the cylinder, 3.25 in., so velocity must have been approximately 63 m. per sec. even with no allowance for the time interval between passing the spark and the start of pressure rise. Flame velocity in the nearly clean combustion space of the engine is comparable with that observed by Fenning (7) when similar mixtures in a clean bomb were ignited by a spark, if allowance be made for differences in dimensions, initial temperature, and pressure. The flame velocity attained in the engine or bomb did not approach that of true detonation and in neither case was there any evidence of that phenomenon.

The pro-knock effect of carbon nuclei.—When hydrocarbon fuels, especially paraffins, are used in an engine, finely divided carbon can be derived from pyrolysis of the fuel, and maximum concentration occurs necessarily in the end gas [Part IV (10)]. Self-ignition can occur accordingly and nearly simultaneously throughout the mass of the gas; this results in detonation knock.

When hydrogen is used as the fuel, finely divided carbon can be obtained from the lubricating oil only and must be distributed by turbulence, more or less uniformly. There can be no preferential concentration in the end gas, consequently the sole effect of the carbon, after the passage of the spark, is to increase flame velocity and thereby promote combustion knock, an effect similar to that obtained by Fenning (7) on igniting electrolytic gas when the time from the passage of the spark to the attainment of maximum pressure was as short as 0.00072 sec., that is, combustion knock was obtained in the bomb on increasing flame speed by using electrolytic gas and in the engine by impregnating hydrogen–air mixtures with finely divided carbon.

Acknowledgments

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